

The University of Chicago

THE SYSTEM
 $\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY AND PALEONTOLOGY

1942

By
JOSEPH SPIVAK

Reprinted from
THE JOURNAL OF GEOLOGY
Vol. LII, No. 1, January-February, 1944

The University of Chicago

THE SYSTEM

$\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY AND PALEONTOLOGY

1942

By
JOSEPH SPIVAK



Reprinted from
THE JOURNAL OF GEOLOGY
Vol. LII, No. 1, January-February, 1944

THE SYSTEM $\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$

JOSEPH SPIVAK
University of Chicago

ABSTRACT

The thermal-equilibrium relationships in the system $\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$ have been investigated by the quenching method. The thermal data are tabulated, and the results are presented in equilibrium diagrams. The bearing of the results of the present study on related systems of the soda-lime-alumina-silica tetrahedron and the petrologic significance are discussed.

INTRODUCTION

This investigation is concerned with the thermal-equilibrium relationships, at atmospheric pressure, of the silicates NaAlSiO_4 , CaSiO_3 , and Na_2SiO_3 . Sodium aluminum orthosilicate and calcium metasilicate constitute the fundamental molecules of the rock-forming minerals nepheline and wollastonite, respectively. Nepheline is a characteristic primary constituent of the alkaline rocks. Wollastonite occurs more typically in metamorphic rocks, but it has been described as a primary constituent of certain alkaline rocks and is associated with nepheline in such occurrences. Both silicates mentioned exhibit polymorphism. The high-temperature modification of NaAlSiO_4 , carnegieite, occurs only in synthetic melts. Pseudowollastonite, the high-temperature modification of CaSiO_3 , has been reported in one unique occurrence in nature.¹ Sodium metasilicate does not occur in nature; it is readily soluble in water, and this property precludes its occurrence as a primary constituent of igneous rocks. The molecule Na_2SiO_3 is considered as a theoretical mineral and is used in the norm system of recalculating rock analyses, when the

soda content exceeds the unit ratio of that alkali to alumina and ferric oxide.²

The system constitutes a portion of a plane within the quaternary system, soda-lime-alumina-silica. This system is of major importance in the physico-chemical aspects of petrologic problems, since the constituent oxides form 83 per cent, by weight, of the average oxide composition of igneous rocks. The quaternary system may be represented by a composition tetrahedron, as shown in Figure 1. The figure also shows the position of the plane within the interior of the tetrahedron and its relationship to other investigated systems which occupy internal positions. The system $\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$ lies in the same plane as the system $\text{CaSiO}_3\text{--CaAlSi}_2\text{O}_8\text{--NaAlSiO}_4$, and the two are adjacent, since the binary system wollastonite-nepheline is common to both. Investigation of the latter system indicated that relationships departed somewhat from true binary behavior as a result of interaction of wollastonite and nepheline to form anorthite.³ This reaction was confirmed by the investigation of the ternary system wollastonite-anorthite-nepheline,⁴

² H. S. Washington, "Chemical Analyses of Igneous Rocks," *U.S. Geol. Surv. Prof. Paper* 99 (1917), p. 1163.

³ W. R. Foster, "The System $\text{NaAlSi}_3\text{O}_8\text{--CaSiO}_3\text{--NaAlSiO}_4$," *Jour. Geol.*, Vol. L (1942), pp. 152-73.

⁴ W. K. Gummer, "The System $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4$," *Jour. Geol.*, Vol. LI (1943), p. 503.

¹ W. F. P. McLintock, "On the Metamorphism Produced by the Combustion of Hydrocarbons in the Tertiary Sediments of Southwest Persia," *Min. Mag.*, Vol. XXIII (1932), pp. 207-26.

which revealed the presence of a maximum temperature on the boundary curve between wollastonite and nepheline at a point which did not lie on the join of the two compounds. As a result, certain

silicate in the high-temperature form, carnegieite. This phenomenon has not been encountered previously in the thermal-equilibrium investigations of silicates.

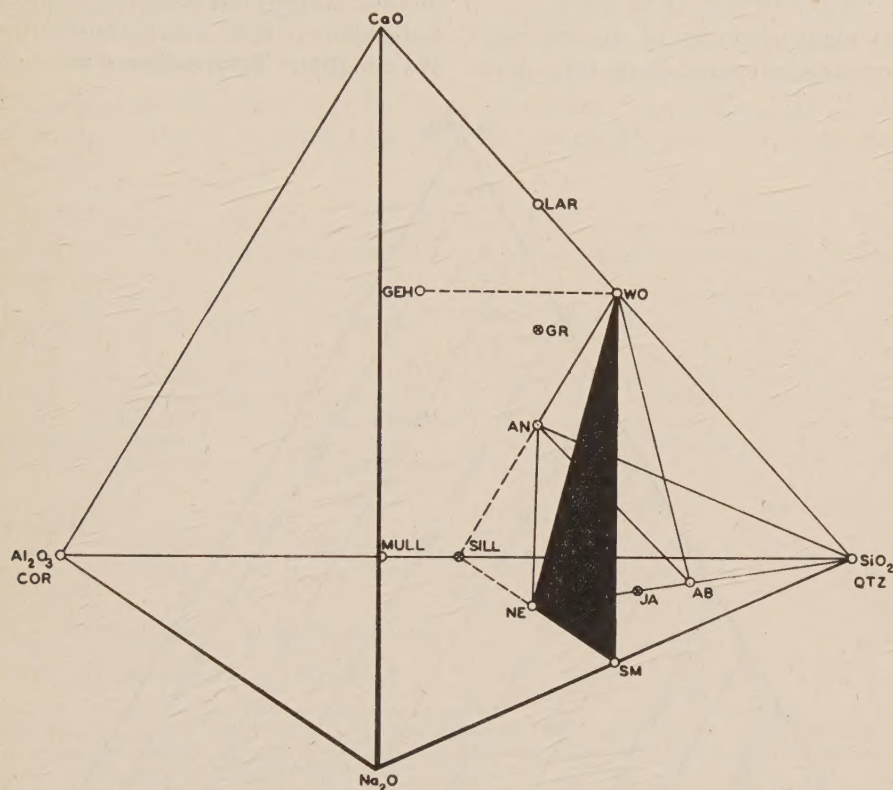


FIG. 1.—The soda-lime-alumina-silica tetrahedron. The shaded area indicates the position of the system nepheline-wollastonite-sodium metasilicate within the tetrahedron. Other internal systems that have been investigated are shown by full lines joining the composition points. The compounds that have been prepared synthetically are shown as $\circ$; those that occur in nature but do not form at liquidus temperatures are shown thus: $\otimes$.

The abbreviations signify: *LAR*, larnite; *WO*, wollastonite; *GEH*, gehlenite; *GR*, grossularite; *AN*, anorthite; *SILL*, sillimanite; *MULL*, mullite; *NE*, nepheline; *SM*, sodium metasilicate; *JA*, jadeite; *QTZ*, quartz; *COR*, corundum; *AB*, albite.

liquids in the area between the maximum and the join did not crystallize within the confines of that system but entered the system $\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$. Another complication results from the limited solid solution of anorthite in the low-temperature modification of NaAlSiO_4 , namely, nepheline, and of sodium meta-

The present investigation was undertaken to determine the courses of crystallization of liquids entering the system nepheline-wollastonite-sodium metasilicate and to obtain experimental data on the unique solid-solution phenomena. Such an investigation is a contribution to the knowledge of the equilibrium rela-

tions in the quaternary system soda-alumina-silica and is a necessary step in the ultimate solution of problems pertaining to igneous rocks.

EXPERIMENTAL PROCEDURE

Sixty-eight mixtures of known composition were prepared from very pure,

terminated in testing for homogeneity, and the results have been plotted on a composition-refractive index diagram (Fig. 2). The mixtures were subjected to thermal study by means of the quenching method, as developed in the Geophysical Laboratory of the Carnegie Institution of Washington.⁵ Temperatures were meas-

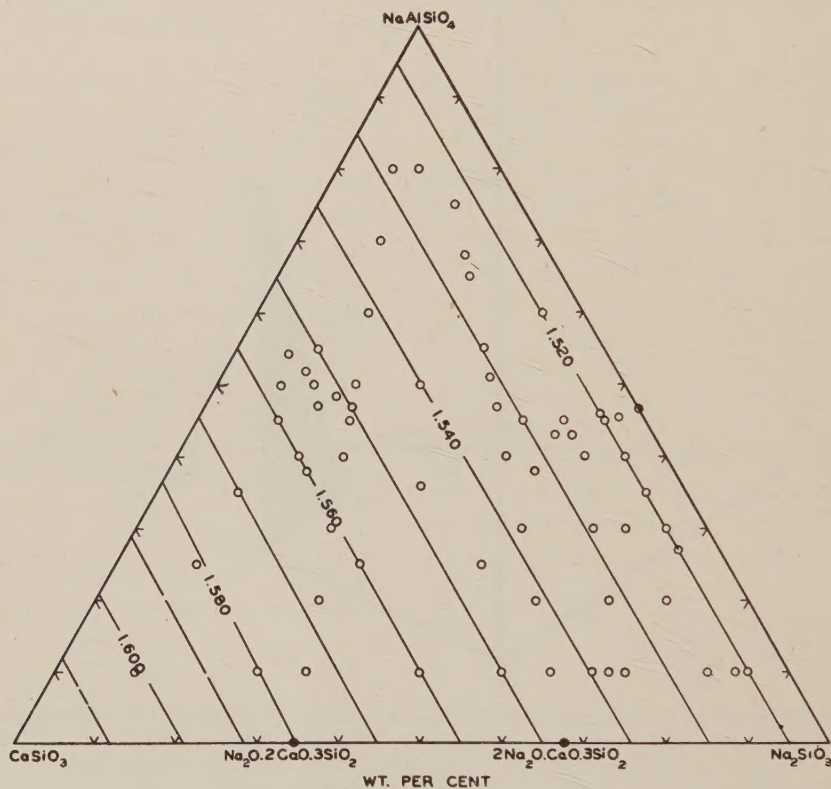


FIG. 2.—The composition-refractive index diagram for the glass mixtures

anhydrous, CaCO_3 , Na_2CO_3 , Al_2O_3 , and SiO_2 . Three to six fusions with intermediate grinding were necessary to insure homogeneity. Each mixture was weighed after each step in preparation, in order to determine the losses due to volatilization of soda. This enabled the control of composition by the addition of Na_2CO_3 , when necessary. The refractive index of each glass was de-

termined with a platinum-platinum 90 rhodium 10 thermoelement calibrated against fixed points, as follows: NaCl , 800.4°C .; gold, $1,062.8^\circ\text{C}$.; lithium metasilicate, $1,201^\circ\text{C}$.; diopside, $1,391.5^\circ\text{C}$.

The results of quenching runs were ex-

⁵ E. S. Shepherd, G. A. Rankin, and F. E. Wright, "The Binary Systems of Alumina with Silica, Lime, and Magnesia," *Amer. Jour. Sci.*, Vol. XXVIII (4th ser., 1909), p. 308.

amined under the petrographic microscope in order to determine the nature of the transformation. The phases were readily distinguished by means of their optical and crystallographic properties. The latter are given in Table 1.

PREVIOUS INVESTIGATIONS

The binary system $\text{NaAlSiO}_4\text{--Na}_2\text{SiO}_3$ was investigated by C. E. Tilley,⁶ and his

of liquids in a portion of the system is somewhat more complicated than in ordinary binary systems. Liquids containing less than 24 per cent of sodium metasilicate will, upon cooling, yield carnegieite mix-crystals which become continuously richer in Na_2SiO_3 . At the requisite temperature, depending upon the initial composition, the liquid will be completely used up; and only car-

TABLE 1
CRYSTALLOGRAPHIC AND OPTICAL PROPERTIES OF THE SOLID PHASES

COMPOUND	CRYSTAL SYSTEM	HABIT	ELONGATION	OPTIC SIGN	REFRACTIVE INDICES			REMARKS
					α	β	γ	
$\alpha\text{-CaSiO}_3\text{.....}$	Pseudo-hexagonal	Plates or laths	—	+	1.610	1.611	1.654*	
$\beta\text{-CaSiO}_3\text{.....}$	Monoclinic	Laths or needles	+	—	1.616	1.629	1.631†	
$\alpha\text{-NaAlSiO}_4\text{...}$	Isometric	Globules		—	1.509		1.514‡	
$\beta\text{-NaAlSiO}_4\text{...}$	Hexagonal	Hexagonal plates or rectangular prisms		—	$\epsilon=1.533$		$\omega=1.537§$	
$\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2\text{.....}$	Pseudo-cubic	Equant grains			1.595		1.598	Twin- ing characteristic
$2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2\text{.....}$	Isometric	Cubes or octahedra			1.571		1.571¶	
$\text{Na}_2\text{SiO}_3\text{.....}$	Orthorhombic	Needles	+	—	1.513	1.520	1.528**	

* J. B. Ferguson and H. E. Merwin, "The Ternary System CaO--MgO--SiO_2 ," *Amer. Jour. Sci.*, Vol. XLVIII (1919), p. 83.

† E. T. Allen, W. P. White, and F. E. Wright, "On Wollastonite and Pseudo-wollastonite-Polymorphic Forms of Calcium Metasilicate," *Amer. Jour. Sci.*, Vol. XXI (1906), p. 108.

‡ N. L. Bowen, "The Binary System, $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ (Nephelinite-Carnegieite)— $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Anorthite)," *Amer. Jour. Sci.*, Vol. XXXIII (1912), pp. 551-73.

§ *Ibid.*, p. 565.

|| G. W. Morey and N. L. Bowen, "The Ternary System, Sodium Metasilicate-Calcium Metasilicate-Silica," *Trans. Soc. Glass Tech.*, Vol. IX (1925), p. 241.

¶ *Ibid.*, p. 240.

** Morey and Bowen, "The Binary System Sodium Metasilicate-Silica," *Jour. Phys. Chem.*, Vol. XXVIII (1924), p. 1175.

equilibrium diagram is shown in Figure 3. This system presents a unique example among investigated silicates, whereby the inversion temperature of a compound is lowered as a result of solid solution in its high-temperature modification. As a result of the solid-solution phenomena, the course of crystallization

negieite solid solutions will exist over a narrow temperature interval. With further cooling, carnegieite will begin to invert to nepheline, the reaction taking place in the solid state. At $1,163^\circ\text{C}$. the temperature will remain constant, with continued cooling, while the remaining carnegieite is being converted to nepheline and liquid. When all the carnegieite is used up, the temperature will fall, and the liquid will yield nepheline crystals

⁶ "The Ternary System, $\text{Na}_2\text{SiO}_3\text{--Na}_2\text{Si}_2\text{O}_5\text{--NaAlSiO}_4$," *Min. u. petrog. Mitt.*, Vol. XLIII (1933), pp. 406-21.

until the eutectic is reached at 906°C . Thus, with continuous cooling, certain liquids will solidify completely and then remelt before the final crystallization temperature is reached.

A mixture having the composition of Tilley's eutectic was prepared by the writer. The liquidus temperature of this

the binary system from the intersection of the liquidus curves and not from a mixture of this composition.

The system $\text{CaSiO}_3\text{--NaAlSiO}_4$ was investigated by Foster,⁷ and the equilibrium diagram based upon his results is shown in Figure 4. The invariant points are given in Table 3.

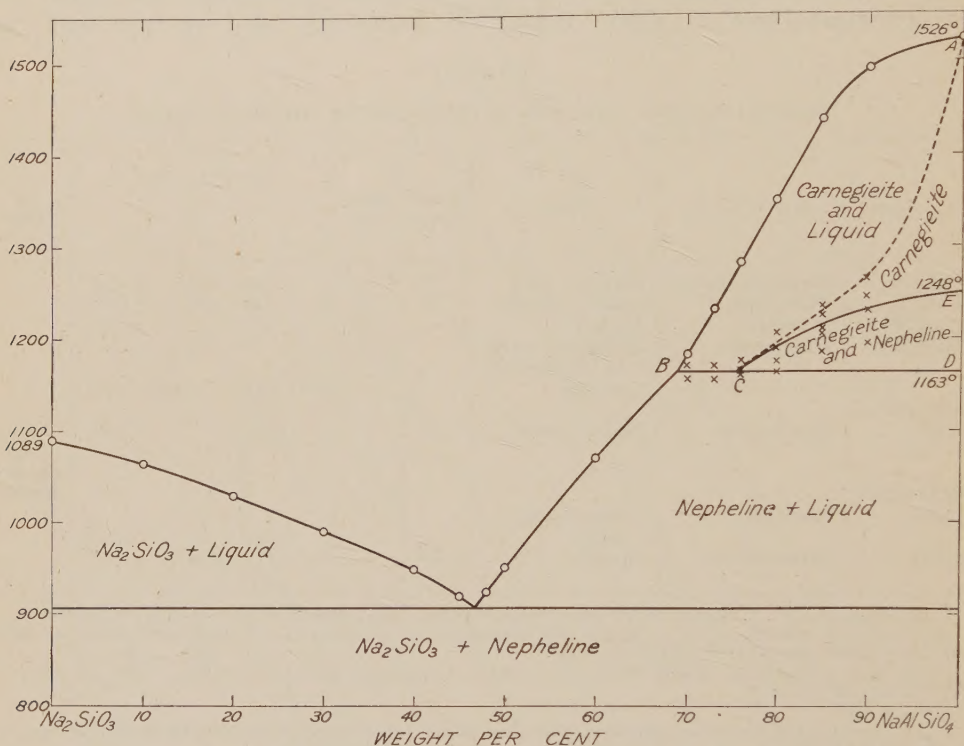


FIG. 3.—Equilibrium diagram for the binary system $\text{NaAlSiO}_4\text{--Na}_2\text{SiO}_3$ (after Tilley)

composition was determined as $907^{\circ} \pm 2^{\circ}\text{C}$., in close agreement with Tilley's result. However, the primary phase of this mixture was sodium metasilicate. The highest temperature at which both phases coexisted was at $900^{\circ} \pm 2^{\circ}\text{C}$. The indicated eutectic temperature is thus slightly lower than that shown by Tilley, and the composition is somewhat richer in nepheline. Tilley located the eutectic temperature and composition in

The system $\text{CaSiO}_3\text{--Na}_2\text{SiO}_3$ was studied by G. W. Morey and N. L. Bowen⁸ in conjunction with the investigation of the melting relations of the soda-lime-silica glasses. The diagram based upon their results is shown in Figure 5, and invariant points are given in Table 3.

⁷ See fn. 3 (1942).

⁸ "The Ternary System, Sodium Metasilicate-Calcium Metasilicate-Silica," *Trans. Soc. Glass Tech.*, Vol. IX (1925), p. 241.

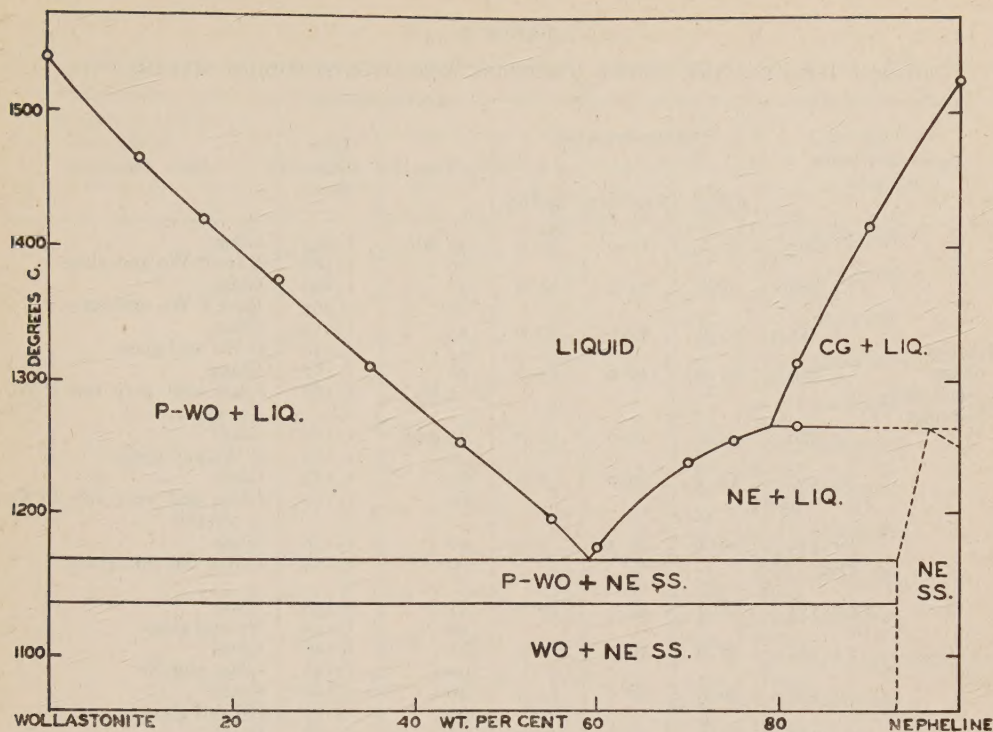


FIG. 4.—Equilibrium diagram for the system CaSiO_3 - NaAlSiO_4 (after Foster)

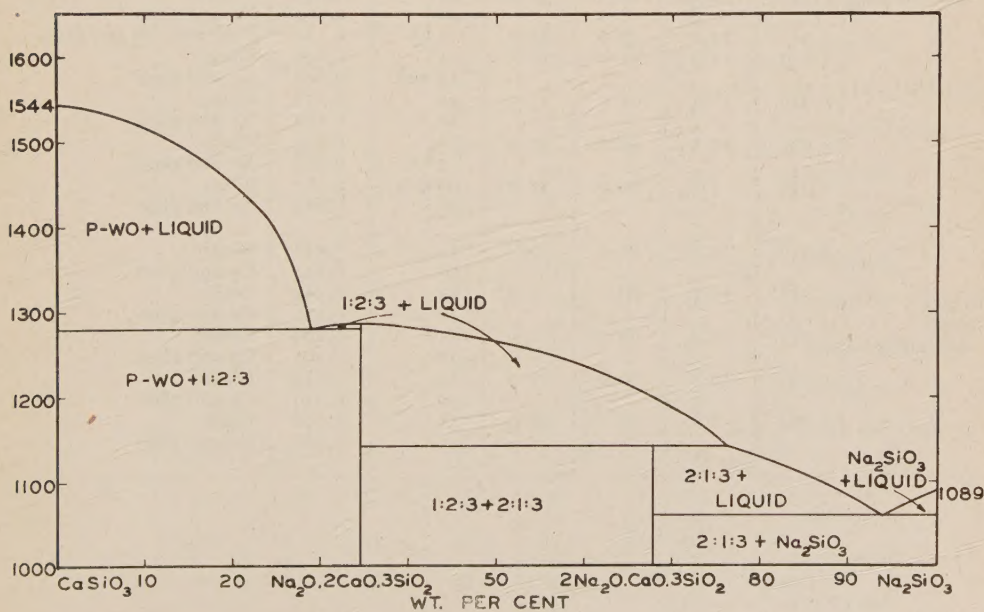


FIG. 5.—Equilibrium diagram for the binary system CaSiO_3 - Na_2SiO_3 (after Morey and Bowen)

TABLE 2

THERMAL DATA FOR THE SYSTEM NEPHELINE-WOLLASTONITE-SODIUM METASILICATE

REFRACTIVE INDEX OF GLASS		WEIGHT PER CENT			TIME	TEMP. (CENTI- GRADE)	FINAL CONDITION
		CaSiO ₃	NaAlSiO ₄	Na ₂ SiO ₃			
Primary- phase pseudowol- lastonite....	1.602	80.0	10.0	10.0	35 min.	1,392°	Glass
					30	1,388	Rare P-Wo and glass
	1.582	65.0	25.0	10.0	45	1,299	Glass
					40	1,295	Rare P-Wo and glass
	1.571	55.0	35.0	10.0	45	1,253	Glass
					45	1,249	P-Wo and glass
	1.560	45.0	40.0	15.0	40	1,162	Glass
					3 hr.	1,158	Glass and very few P-Wo crystals
	1.560	45.0	45.0	10.0	35 min.	1,180	Glass
					30	1,176	P-Wo and glass
Primary- phase nepheline....	1.557	42.0	50.0	8.0	60	1,174	Glass
					60	1,170	Glass and very few P-Wo crystals
	1.550	39.4	54.3	6.3	90	1,158	Glass
					60	1,154	P-Wo, Ne, and glass
	1.553	38.0	52.0	10.0	45	1,158	Glass
					45	1,154	Ne and glass
	1.555	38.0	50.0	12.0	45	1,146	Glass
					90	1,142	Glass and Ne
	1.550	36.0	48.5	15.5	40	1,129	Glass
					90	1,125	Ne and glass
	1.550	35.0	55.0	10.0	45	1,166	Glass
					40	1,162	Ne and glass
	1.547	32.9	50.0	17.1	45	1,137	Glass
					45	1,133	Glass and Ne
	1.546	26.2	60.0	13.8	45	1,193	Glass
					40	1,189	Ne and glass
	1.541	25.0	50.0	25.0	2 hr.	1,112	Very rare Ne and glass
	1.530	14.7	55.0	30.3	2	1,096	Glass
Primary- phase carnegieite..					45 min.	1,092	Ne and glass
	1.527	11.5	65.0	23.5	45	1,176	Glass
					40	1,172	Ne and glass
	1.525	10.0	45.0	45.0	60	1,029	Glass
					2 hr.	1,025	Ne and glass
	1.520	5.0	60.0	35.0	90 min.	1,087	Glass
					55	1,083	Ne and glass
	1.536	19.8	70.0	10.2	45	1,248	Glass
					50	1,244	Cg and glass
	1.528	13.0	80.0	7.0	35	1,345	Glass
					40	1,341	Cg and glass
Primary- phase carnegieite..	1.525	10.4	68.0	21.6	45	1,206	Glass
					70	1,202	Cg and glass
	1.525	10.0	80.0	10.0	35	1,343	Glass
					30	1,339	Cg and glass
	1.524	8.1	75.0	16.9	35	1,290	Glass
					45	1,286	Cg and glass

TABLE 2—Continued

REFRACTIVE INDEX OF GLASS		WEIGHT PER CENT			TIME	TEMP. (CENTI- GRADE)	FINAL CONDITION
		CaSiO_3	NaAlSiO_4	Na_2SiO_3			
Primary-phase $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$	I. 580	65.0	10.0	25.0	45 min. 105	I, 253° I, 249	Glass I: 2: 3 and glass
	I. 575	59.0	10.0	31.0	35 40	I, 258 I, 254	Glass I: 2: 3 and glass
	I. 568	52.5	20.0	27.5	35 40	I, 229 I, 225	Glass I: 2: 3 and glass
	I. 562	46.0	30.0	24.0	60 40	I, 200 I, 196	Glass I: 2: 3 and glass
	I. 560	45.0	10.0	45.0	40 35	I, 239 I, 235	Glass I: 2: 3 and glass
	I. 561	45.0	25.0	30.0	40 45	I, 212 I, 208	Glass I: 2: 3 and glass
	I. 560	45.0	38.0	17.0	40 45	I, 158 I, 154	Glass I: 2: 3 and glass
	I. 554	39.5	40.0	20.5	45 60	I, 154 I, 150	Glass I: 2: 3 and glass
	I. 555	39.0	47.0	14.0	45 100	I, 125 I, 123	Glass I: 2: 3 and glass
	I. 550	36.1	45.0	18.9	45 50	I, 136 I, 132	Glass I: 2: 3 and glass
	I. 551	34.8	47.0	18.2	45 110	I, 129 I, 127	Glass Very rare I: 2: 3 and glass
	I. 550	35.0	10.0	55.0	50 45	I, 222 I, 218	Glass I: 2: 3 and glass
	I. 551	32.0	36.0	32.0	35 35	I, 179 I, 175	Glass Rare I: 2: 3 and glass
	I. 545	30.0	25.0	45.0	45 40	I, 175 I, 171	Glass I: 2: 3 and glass
	I. 544	29.0	10.0	61.0	40 45	I, 179 I, 175	Glass I: 2: 3 and glass
	I. 542	25.8	20.0	54.2	45 45	I, 175 I, 160	Glass I: 2: 3 and glass
	I. 540	24.0	10.0	66.0	40 50	I, 147 I, 145	Glass Very rare I: 2: 3 and glass
	I. 537	22.5	30.0	47.5	50 65	I, 137 I, 133	Glass Rare I: 2: 3 and glass
	I. 537	22.0	10.0	68.0	60 75	I, 133 I, 129	Glass I: 2: 3 and glass
	I. 535	19.5	40.0	40.5	45 55	I, 109 I, 105	Glass I: 2: 3 and glass
	I. 532	17.2	47.0	35.8	60 45	I, 088 I, 084	Glass I: 2: 3 and glass
	I. 532	17.0	38.0	45.0	60 3 hr.	I, 100 I, 096	Glass I: 2: 3 and glass
	I. 530	17.0	20.0	63.0	60 min. 45	I, 101 I, 097	Glass I: 2: 3 and glass
	I. 530	15.0	45.0	40.0	45 3 hr.	I, 078 I, 074	Glass I: 2: 3 and glass
	I. 532	15.8	51.0	33.2	40 min. 3 hr.	I, 076 I, 072	Glass Rare I: 2: 3 and glass
	I. 530	14.0	30.0	56.0	65 min. 60	I, 076 I, 072	Glass Rare I: 2: 3 and glass
	I. 527	12.0	43.0	45.0	70 50	I, 053 I, 049	Glass I: 2: 3 and glass
	I. 525	10.0	43.0	47.0	55 105	I, 011 I, 007	Glass I: 2: 3 and glass
	I. 525	10.0	40.0	50.0	60 40	I, 026 I, 022	Glass I: 2: 3 and glass

TABLE 2—Continued

REFRACTIVE INDEX OF GLASS		WEIGHT PER CENT			TIME	TEMP. (CENTI- GRADE)	FINAL CONDITION
		CaSiO ₃	NaAlSiO ₄	Na ₂ SiO ₃			
Primary-phase 2Na ₂ O·CaO· 3SiO ₂	I. 535	20.0	10.0	70.0	2 hr.	1,112°	Glass
					40 min.	1,108	2:1:3 and glass
	I. 525	10.0	30.0	60.0	40	1,039	Glass
					135	1,035	2:1:3 and glass
	I. 526	10.0	20.0	70.0	50	1,048	Glass
					55	1,044	2:1:3 and glass
	I. 525	10.0	10.0	80.0	40	1,052	Glass
					35	1,048	2:1:3 and glass
	I. 521	5.0	46.0	49.0	55	933	Glass
					90	929	2:1:3 and glass
	I. 521	5.0	45.0	50.0	1 hr.	940	Glass
					50 min.	936	2:1:3 and glass
	I. 520	5.0	40.0	55.0	1 hr.	949	Very rare 2:1:3 and glass
	I. 520	5.0	35.0	60.0	75 min.	958	Glass
Primary-phase sodium metasilicate.					60	954	2:1:3 and glass
	I. 520	5.0	30.0	65.0	3 hr.	973	Glass
					45 min.	969	2:1:3 and glass
	I. 520	5.0	27.0	68.0	1 hr.	977	Glass
					2	973	2:1:3, SM, and glass
	I. 517	3.0	45.5	51.5	1	902	Glass
					75 min.	896	2:1:3 and glass
	I. 520	6.5	10.0	83.5	150	1,036	Glass
					45	1,032	SM and glass
Nepheline- carnegieite inversion....	I. 520	5.0	10.0	85.0	45	1,053	Glass
					70	1,049	SM and glass
	I. 521	5.0	27.0	68.00	1 hr.	977	Glass
					2	973	SM, 2:1:3, and glass
	I. 515		46.75	53.25	1	909	Glass
					75 min.	905	SM and glass
	I. 528	13.0	80.0	7.0	16 hr.	1,228	Ne and glass
					14½	1,233	Ne, Cg, and glass
					17	1,238	Cg, Ne, and glass
Wollastonite- pseudowol- lastonite inversion....					11	1,241	Cg and glass
	I. 536	19.8	70.0	10.2	16	1,228	Ne and glass
					14½	1,233	Ne, very rare Cg, and glass
					17	1,238	Cg, very rare Ne, and glass
					11	1,241	Cg and glass
	I. 524	8.1	75.0	16.9	15½	1,190	Ne and glass
					22	1,197	Ne, very rare Cg, and glass
					16	1,202	Ne, Cg, and glass
					11	1,208	Cg and glass
	I. 525	10.4	68.0	21.6	13	1,190	Ne and glass
Primary-phase nepheline....					16	1,194	Ne, Cg, and glass
					16	1,197	Ne, Cg, and glass
					70 min.	1,202	Cg and glass
Wollastonite- pseudowol- lastonite inversion....	I. 571	55.0	35.0	10.0	24 hr.	1,119	Wo and glass
					17	1,125	Wo, P-Wo, and glass
					18	1,127	Wo, P-Wo, and glass
Primary-phase nepheline....	I. 537	5.0	60.0	35.0	75 min.	1,318	Very rare Ne and glass

THE THERMAL INVESTIGATION

Thermal data necessary for establishing the equilibrium relationships in the system are shown in Table 2, and the diagrams based upon these results are shown in Figures 6 and 7. In the diagrams small circles indicate the compositions of mixtures that were investi-

ure 6 the nature of this liquidus surface may be inferred from the position of the isotherms which are spaced at temperature intervals of 50°C . Figure 7 shows the stability fields of each solid phase, with the isotherms omitted and with arrows indicating the directions of falling temperatures.

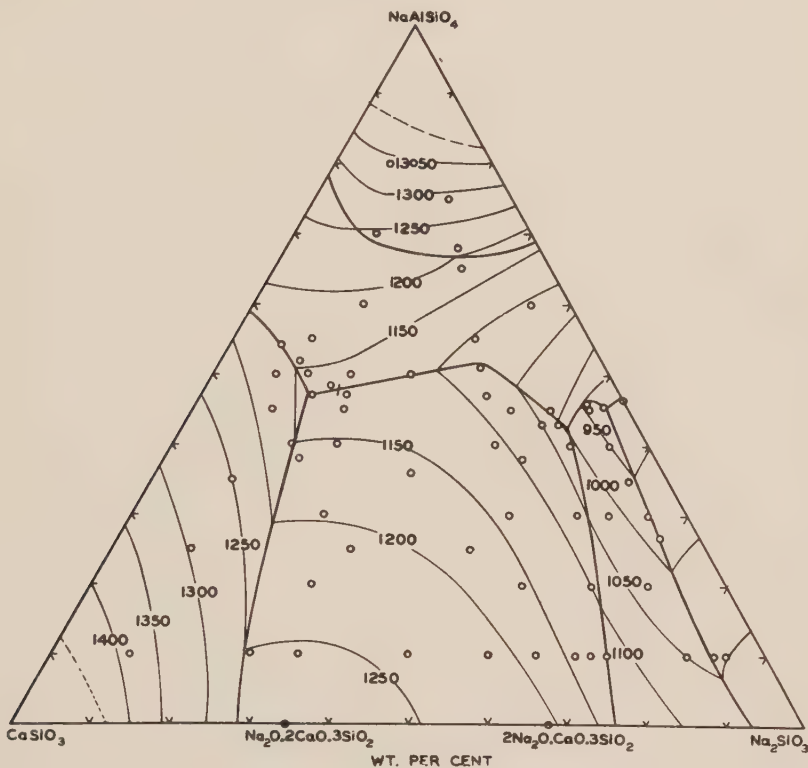


FIG. 6.—Equilibrium diagram for the system NaAlSiO_4 - CaSiO_3 - Na_2SiO_3 with isotherms

gated. The abbreviations used in the tables and in the discussion of the system are as follows: P-Wo—pseudowollastonite; Wo—wollastonite; Ne—nepheline; Cg—carnegieite; 1:2:3— $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$; 2:1:3— $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$; SM—sodium metasilicate.

A ternary equilibrium diagram represents the projection of the liquidus surface upon the triangular base of a solid temperature-composition model. In Fig-

The boundary curves divide the system into six fields. In the order of decreasing size they are the fields of the 1:2:3 compound, pseudowollastonite, nepheline solid solutions, carnegieite solid solutions, the 2:1:3 compound, and sodium metasilicate. Wollastonite occupies a seventh field, but the areal extent of the latter is too small to be shown adequately in the diagrams. The boundary curve separating the field of wollastonite

within the quaternary system soda-lime-alumina-silica when plotted on a weight per cent basis. The internal plane of the tetrahedron has at its apexes the compounds Al_2SiO_5 (sillimanite), CaSiO_3

ed by Gummer,⁹ but it can be completely understood only in the light of the work on the adjacent portion as here investigated. Indeed, it was to accomplish this end that the present investigation was

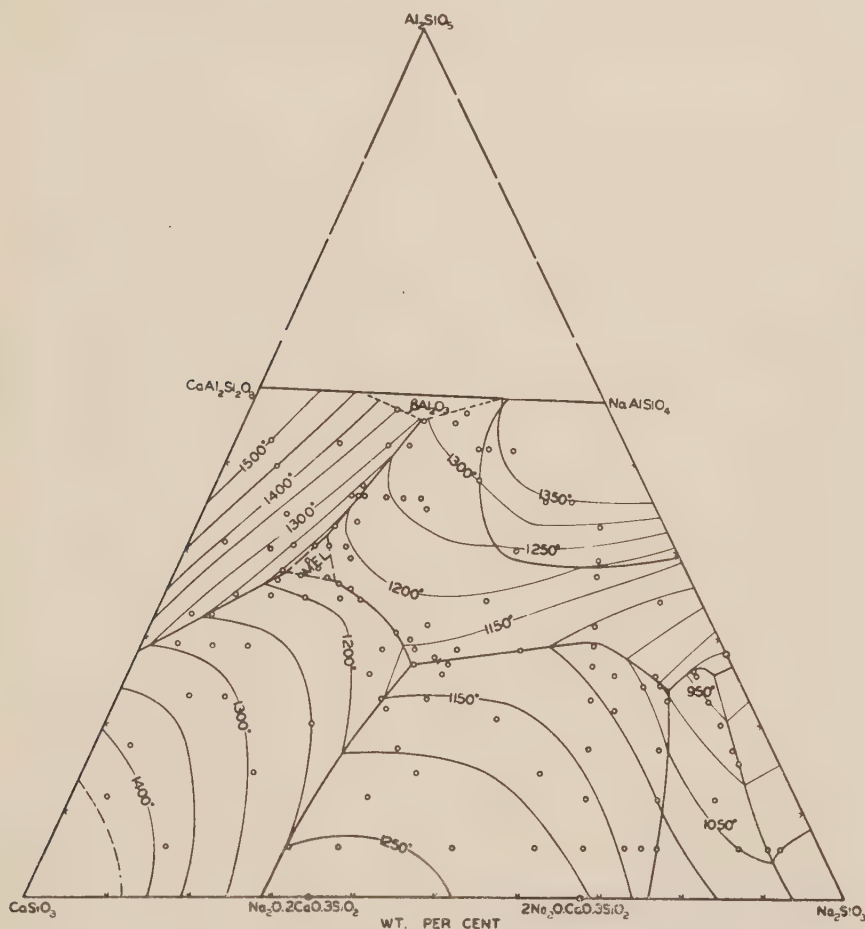


FIG. 8.—The section through the tetrahedron (cf. Fig. 1) showing the phase relations in the system wollastonite-anorthite-nepheline-sodium metasilicate. The triangle is not equilateral because compositions are plotted in weight per cent of the oxides. The abbreviation *MEL* signifies melilite.

(wollastonite, pseudowollastonite), and sodium metasilicate. The upper portion of the triangle has not been investigated, for sillimanite does not form at melting temperatures in mixtures of this system. The wollastonite-anorthite-nepheline portion of this plane has been investigat-

undertaken. This combined system will be discussed in detail in a later section.

The system nepheline-wollastonite-sodium metasilicate has five ternary invariant points, of which only three are shown in the equilibrium diagrams. In

⁹ See ft. 4 (1943).

Figure 7 the invariant point *E* is a ternary eutectic at which the crystalline phases wollastonite, nepheline solid solution, and 1:2:3 coexist with liquid. Similarly, *E*₁ is a ternary eutectic at which the crystalline phases 2:1:3, sodium metasilicate, and nepheline solid solution

tonite. The invariant points, together with the composition of the phases and their respective temperatures, are listed in Table 3.

The join between the 1:2:3 compound and NaAlSiO₄ is not a true binary system, since the temperature at which the

TABLE 3
INVARIANT POINTS

CRYSTALLINE PHASES	COMPOSITION OF LIQUID PHASE IN WEIGHT PER CENT			TYPE	TEMPERATURE (CENTIGRADE)
	CaSiO ₃	NaAlSiO ₄	Na ₂ SiO ₃		
α -CaSiO ₃	100			Melting	1,544*
α -CaSiO ₃ and β -CaSiO ₃	100††			Inversion	1,125±2
α -NaAlSiO ₄		100		Melting	1,526†
α -NaAlSiO ₄ and β -NaAlSiO ₄		100††		Inversion	1,254±5‡
Na ₂ SiO ₃			100	Melting	1,089§
Na ₂ O·2CaO·3SiO ₂	65.5		34.5	Melting	1,284
α -CaSiO ₃ and NaAlSiO ₄	41.0	59.0		Pseudo- eutectic	1,164¶
α -CaSiO ₃ and 1:2:3.....	71.4		28.6	Eutectic	1,280**
1:2:3 and 2:1:3.....	23.8		76.2	Reaction point	1,141
1:2:3 and Na ₂ SiO ₃	6.2		93.8	Eutectic	1,060
Na ₂ SiO ₃ and NaAlSiO ₄		47.0	53.0	Eutectic	900±2
Wo, 1:2:3, Ne (containing 8 per cent An)...	39.4	47.0	13.6	Eutectic	1,120±3
SM, 2:1:3, Ne (containing approximately 1 per cent An).....	2.8	45.4	51.8	Eutectic	892±2
1:2:3, 2:1:3, Ne (containing 5 per cent An)...	8.8	42.5	47.8	Reaction point	985±8
P-Wo, Wo, Ne (containing over 7 per cent An)...	39.5	47.5	13.0	Inversion	1,125±2
P-Wo, Wo, 1:2:3.....	40.0	46.5	13.5	Inversion	1,125±2

* E. F. Osborn and J. F. Schairer, "The Ternary System Pseudowollastonite-Akermanite-Gehlenite," *Amer. Jour. Sci.*, Vol. CXXXIX (1941), pp. 715-63.

† N. L. Bowen, "The Binary System: Na₂Al₂Si₂O₈ (Nephelinite-Carnegieite)—CaAl₂Si₂O₈ (Anorthite)," *Amer. Jour. Sci.*, Vol. XXXIII (1912), pp. 551-73.

‡ J. W. Greig and Tom W. F. Barth, "The System, Na₂O·Al₂O₃·2SiO₂ (Nephelinite-Carnegieite)—Na₂O·Al₂O₃·6SiO₂ (Albite), *Amer. Jour. Sci.*, Vol. XXXV-A (1938), p. 108.

§ F. C. Kracek, "The System Sodium Oxide-Silica," *Jour. Phys. Chem.*, Vol. XXXIV (1930), pp. 1583-98.

|| G. W. Morey and N. L. Bowen, "The Ternary System, Sodium Metasilicate-Calcium Metasilicate-Silica," *Trans. Soc. Glass Tech.*, Vol. IX (1925), p. 264.

¶ W. R. Foster, "The System NaAlSi₃O₈-CaSiO₃-NaAlSiO₄," *Jour. Geol.*, Vol. L (1942), p. 160.

** Morey and Bowen, *op. cit.* Table 2, ref. No. 2802B, p. 238.

†† Composition of solid phases; no liquid phase present.

coexist with liquid. The point *R* is a ternary reaction point, at which the crystalline phases 1:2:3, 2:1:3, and nepheline solid solution coexist with liquid. The other two invariant points are not shown in the diagram but represent the inversion points at which pseudowollastonite is transformed to wollas-

two phases coexist is not a maximum temperature on the boundary curve between the two fields. The position of the maximum temperature on the boundary curve is at 35.5 per cent wollastonite and at a temperature of 1,128° C., as shown in Figure 7. This temperature is only slightly higher than the temperature on

the boundary curve at its intersection with the $\text{NaAlSiO}_4\text{--}1:2:3$ join. In fact, the temperature gradient along the boundary curve between the ternary eutectic E and the $\text{NaAlSiO}_4\text{--}1:2:3$ join is very small. The thermal relations were definitely established by making multiple quenching runs, that is, putting charges of two or three mixtures in together and holding them at the requisite temperatures, so that the thermal conditions were identical for each charge, and then comparing the phase changes in each mixture. Further evidence of the position of the maximum temperature on the boundary curve was obtained by comparing the proportions of the crystalline phases present after complete devitrification of the appropriate mixtures. It was found that the mixture whose composition lies close to the maximum temperature contained only a trace of wollastonite in the crystalline product. The presence of this maximum temperature on the boundary curve indicates that pure nepheline does not occur within the ternary system; in other words, if any CaO is present in the liquid, some of it will enter as anorthite into the nepheline mix-crystals.

THE NEPHELINE-CARNEGIEITE INVERSION

The boundary curve between nepheline and carnegieite is univariant but is not an isotherm, since the temperature of the transformation is different in each limiting system. In the system wollastonite-nepheline the inversion temperature of the latter is raised above that of the pure compound as a result of solid solution of anorthite in nepheline. The amount of solid solution in carnegieite, the high temperature form, is negligible. On the other hand, the inversion temperature of nepheline is lowered considerably in the system nepheline-sodium metasilicate, because there is solid solution of

sodium metasilicate in carnegieite but not in nepheline. The presence of two different compounds in solid solution in the low and high temperature forms of NaAlSiO_4 , introduces considerable complexity into the inversion phenomena.

In order to facilitate discussion of the inversion phenomena, it is necessary to consider the thermal data for the system nepheline-anorthite. This system was first investigated by Bowen, and later additions were made as a result of investigations by Schairer and by Gummer.¹⁰ The equilibrium diagram is shown in Figure 9. Nepheline can take as much as 35 per cent of anorthite into solid solution, whereas carnegieite solid solutions contain less than 5 per cent of anorthite. The inversion temperature of nepheline to carnegieite is $1,352^\circ\text{C.}$, an increase of 104° above that of the pure compound; this increase is due to the solid solution of anorthite in nepheline. Recent investigations by Schairer and by Gummer in related systems have shown that the field of β -alumina encroaches upon this system, and in consequence the binary nature of the equilibrium is destroyed. The liquidus for β -alumina has not been definitely established as yet, but its tentative outline is shown in the diagram.

The inversion phenomena are considered in terms of the system wollastonite-anorthite-nepheline-sodium metasilicate, since this is necessary in order to express the composition of the nepheline and carnegieite solid solutions. The inversion curve is shown in Figure 10 and is based upon the data of Table 2 and upon information obtained from Gummer's study. This is the boundary curve

¹⁰ Bowen, "The Binary System NaAlSiO_4 (Carnegieite, Nepheline)— $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Anorthite)," *Amer. Jour. Sci.*, Vol. XXXIII (4th ser., 1912), pp. 551-73; J. F. Schairer, unpublished data; Gummer, see fn. 4 (1943).

between the fields of nepheline and carnegieite, and the temperature falls along the curve from a maximum of $1,352^{\circ}\text{C}.$, on the anorthite-nepheline join, to a minimum of $1,163^{\circ}\text{C}.$, on the sodium metasilicate-nepheline join. The temperature gradient along the boundary curve is rather uniform but decreases somewhat at lower temperatures.

A liquid on the boundary curve will be in equilibrium with a nepheline solid

figuration and areal extent of the field of ternary solid solutions is inferred, for no compositions were studied in that area. The limit of nepheline solid solution at the inversion temperature in the system nepheline-anorthite is shown by a brace. The composition of the coexisting phases at any temperature can be read from the diagram—for example, a liquid having the composition s , at a temperature of $1,208^{\circ}\text{C}.$, will be in

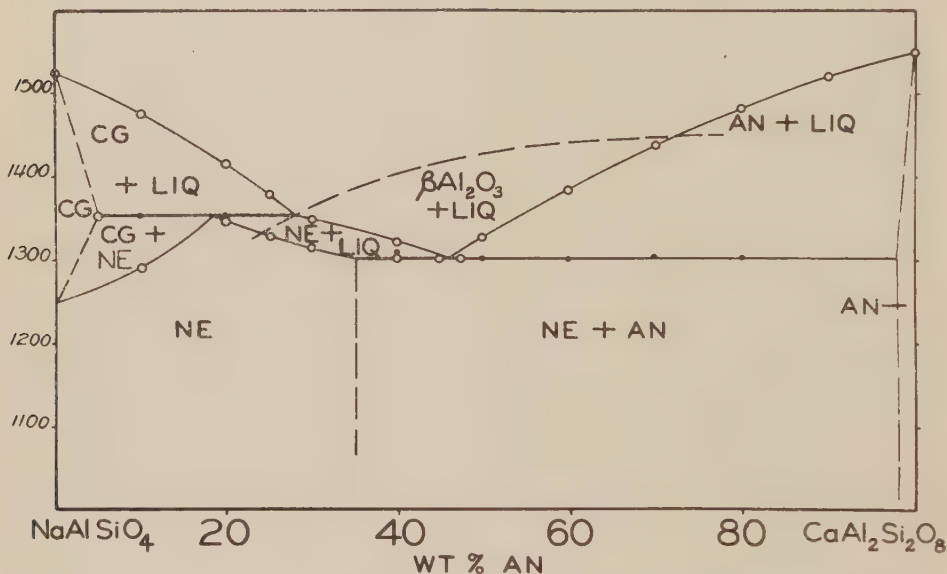


FIG. 9.—Phase relations in the system $\text{NaAlSiO}_4\text{--CaAl}_2\text{Si}_2\text{O}_8$ (after Bowen, with modifications by Schairer and Gummer).

solution and a carnegieite solid solution at a fixed temperature. Nepheline solid solutions will contain anorthite only. Carnegieite can take sodium metasilicate and a small amount of anorthite into solid solution, so that there is an area of ternary solid solutions in the system, and this is shown as the area $\text{NaAlSiO}_4\text{--}A\text{--}B$, in the diagram. The limits of the area of ternary solid solutions are determined by the equilibrium data derived from the appropriate binary or pseudo-binary diagrams and are indicated in the figure by braces along the side lines. The con-

equilibrium with a nepheline solid solution, containing 2 per cent anorthite, and with carnegieite U , containing 11 per cent sodium metasilicate and less than 1 per cent of anorthite in solid solution. The occurrence of a liquid in equilibrium with both nepheline and carnegieite solid solutions does not mean that the inversion will take place completely at that temperature. Upon reaching the boundary curve under cooling conditions, a liquid whose initial composition is in the field of carnegieite, will be in equilibrium with nepheline and carnegieite solid solutions;

but the inversion to nepheline will take place over a temperature interval, and during this transformation the composition of the liquid will move along the boundary curve, while the composition of both nepheline and carnegieite and their proportions change until the latter is used up.

THE $1,300^\circ\text{C.}$ ISOTHERM

Figure 11 shows the phase relations at a temperature of $1,300^\circ\text{C.}$, at which the largest area in the system is occupied by one phase, namely, liquid. Adjacent to this one-phase area there are a series of alternating two- and three-phase areas in which one solid phase is in equilibrium

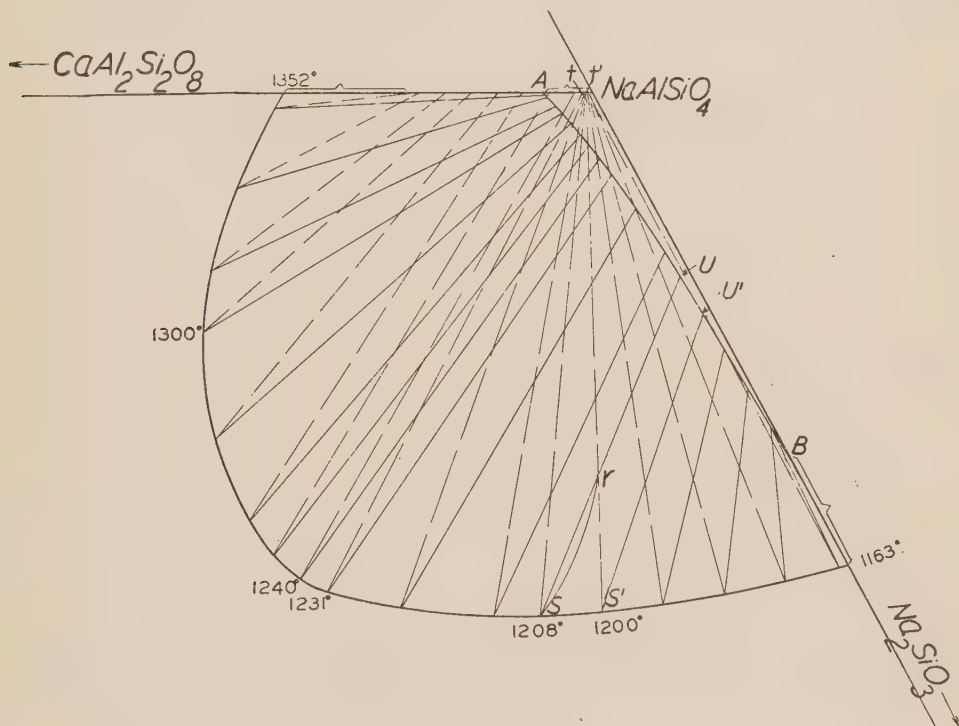


FIG. 10.—The nepheline-carnegieite boundary curve in the system wollastonite-anorthite-nepheline-sodium metasilicate, showing inversion temperatures at determined points and the tie lines or three-phase boundaries of nepheline and carnegieite solid solutions.

A SERIES OF ISOTHERMAL PLANES

In order to depict the equilibrium relations and the compositions of all the phases within the system, it is convenient to consider a series of isothermal planes. These diagrams are drawn to scale; and the composition of all the phases are determined from experimental results of the present investigation, supplemented by data from the related binary systems and the adjoining system wollastonite-anorthite-nepheline.

with liquid or two solid phases are in equilibrium with liquid. At this temperature no three-solid-phase triangles occur within the system.

Pseudowollastonite is in equilibrium with liquids *a* to *b*, and all mixtures in the area *a-b*– CaSiO_3 consist, at $1,300^\circ\text{C.}$, of pseudowollastonite and liquid whose composition is given by the tie-line from CaSiO_3 passing through the point indicating the total composition of the mixture.

The liquid *b* is in equilibrium with both pseudowollastonite and anorthite and is therefore a point in the boundary curve between the fields of these two phases.

Anorthite is in equilibrium with liquids *b* to *c*. All mixtures in the area $\text{CaAl}_2\text{Si}_2\text{O}_8$ -*b*-*c* consist of anorthite and liquid whose composition is given by the tie-line passing through the point in-

negieite *i*. Liquid *e* is therefore a point in the boundary curve between the fields of nepheline and carnegieite. All mixtures lying in this triangle consist of these three phases at $1,300^\circ\text{C}$.

The area *h**j**k**i* contains mixtures which are completely crystalline at this temperature and consist of nephelines *h* to *j* in equilibrium with carnegieites *k* to *i*. The limiting equilibrium of the area *jk*

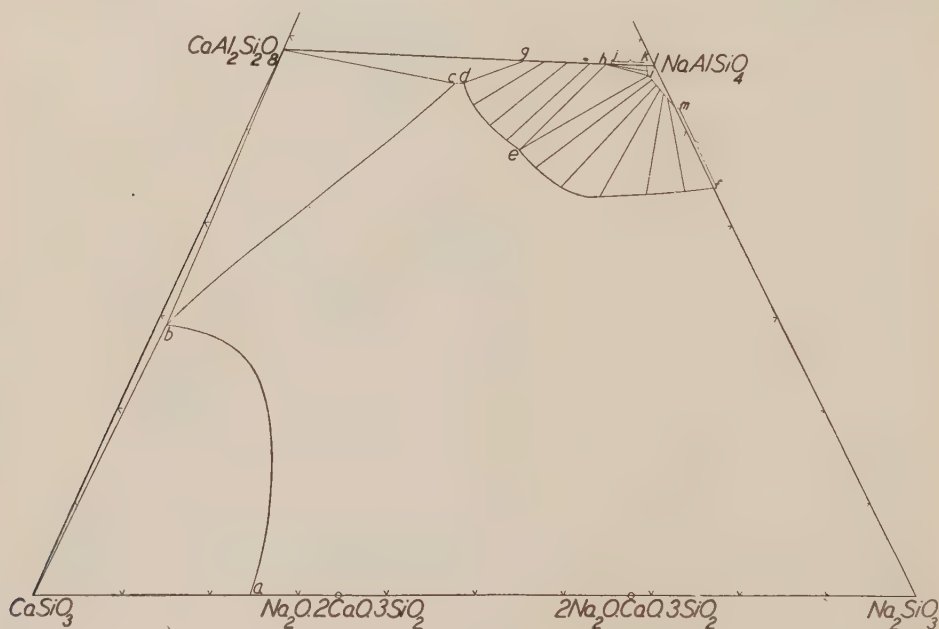


FIG. 11.—Phase relations at $1,300^\circ\text{C}$.

dicating the total composition of the mixture.

The area enclosed by the quadrilateral anorthite-*c*-*d*-*g* ($\text{Ne}_{65}\text{An}_{35}$) contains the field of β -alumina, which exhibits quaternary equilibrium. The phase relations of this compound cannot be discussed here.

The liquids *d* to *e* are in equilibrium with nepheline solid solutions *g* to *h*. All mixtures in this area consist of liquid and nepheline solid solution.

The triangle *ehi* is a three-phase area in which the liquid of composition *e* is in equilibrium with nepheline *h* and car-

negieite *i*. Liquid *e* is therefore a point in the boundary curve between the fields of nepheline and carnegieite. All mixtures lying in this triangle consist of these three phases at $1,300^\circ\text{C}$.

The area *h**j**k**i* contains mixtures which are completely crystalline at this temperature and consist of nephelines *h* to *j* in equilibrium with carnegieites *k* to *i*. The limiting equilibrium of the area *jk* is obtained from the binary diagram (Fig. 9) and is indicated by a brace.

The liquids *e* to *f* are in equilibrium

with carnegieite solid solutions *i* to *m*. The limiting equilibrium *mf* is binary and is shown by the brace connecting the two phases.

THE 1,200° C. ISOTHERM

The equilibrium relations at this temperature are shown in Figure 12. The properties of the alternating two- and three-phase areas in a large part of the

hinl are completely crystalline and consist of carnegieite solid solutions between *i* and *n*, in equilibrium with nepheline solid solutions *h* to *l*. The tie-line *ln* represents binary equilibrium. The liquids *e* to *f* are in equilibrium with carnegieites varying in composition from *i* to *m*, each joined by the appropriate tie-line. The tie-line *mf* again represents binary equilibrium as indicated by the brace.



FIG. 12.—Phase relations at 1,200° C. The lettering in the distorted diagram Fig. 12 (a) corresponds with that of the true scale figure.

system are, at this temperature, similar to those already described and require no further mention.

The areas close to the nepheline-sodium metasilicate join differ slightly and will be discussed with the aid of a distorted diagram, Figure 12 (a). The one-phase area of ternary solid solutions *nim* has decreased considerably in size. This area is determined by the equilibrium relations in the binary system nepheline-sodium metasilicate, at 1,200° C., and by the relations shown in Figure 10 at the same temperature. Mixtures in the area

THE 1,164° C. ISOTHERM

As shown in Figure 13, this is the temperature of the (pseudo-)eutectic of the system wollastonite-nepheline. A large portion of the system wollastonite-anorthite-nepheline is crystalline at this temperature. All mixtures lying in the triangle pseudowollastonite-anorthite-*g* ($\text{Ne}_{65}\text{An}_{35}$) are completely solid and consist of these three phases in proportions which may be determined by the geometrical relations of the composition point in that area. Mixtures in the triangle pseudowollastonite-*g*-*q* are completely

solid and consist of pseudowollastonite and a nepheline solid solution.

In discussing the solid-phase triangles, it is assumed that there is no change in the amount of anorthite soluble in nepheline, with falling temperatures. This is the equilibrium relation as indicated in the system nepheline-anorthite (Fig. 9). One three-phase boundary determination

vary with changes of temperature, for a different nepheline solid solution would be in equilibrium with the two other solid phases at different temperatures, and its composition would be determined by the solidus relations in the system anorthite-nepheline.

Liquid *p* is in equilibrium with pseudowollastonite and nepheline *q*. The point

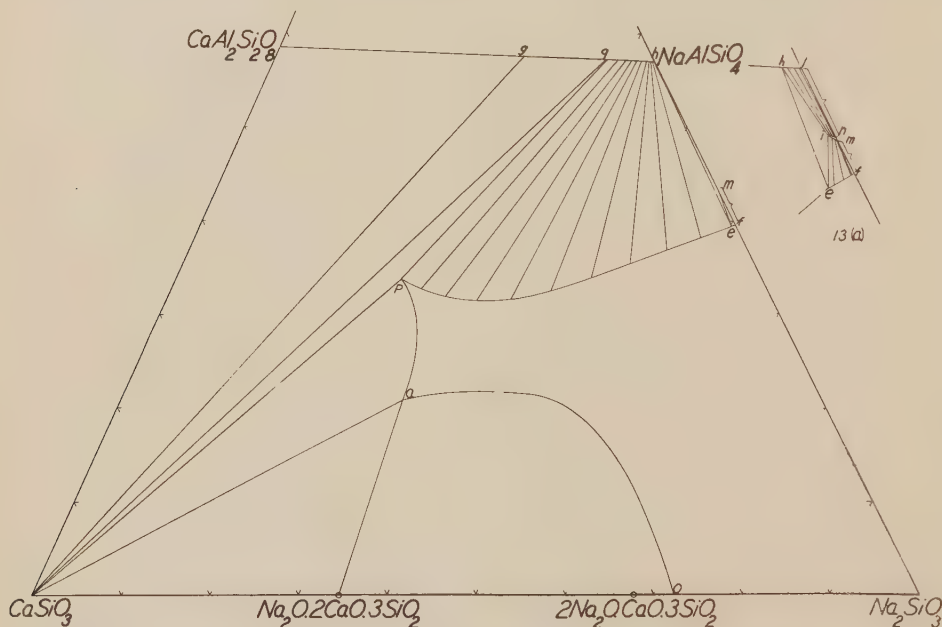


FIG. 13.—Phase relations at 1,164° C. The inset Fig. 13 (a) is distorted to show the relations in the carnegieite field.

made by the writer in the system wollastonite-anorthite-nepheline indicated that the nepheline solid solution contained 30 per cent anorthite at a temperature of 1,250° C. There is a possibility that the solubility of anorthite in nepheline decreases with falling temperatures, although there is insufficient evidence to establish this relation conclusively. If there is decreasing solubility of anorthite in nepheline, then the three-solid-phase triangles—such as the area pseudowollastonite-anorthite-nepheline(*g*)—would

p is the pseudo-eutectic in the “binary” system $\text{CaSiO}_3\text{--NaAlSiO}_4$.

Liquids *p* to *e* are in equilibrium with nephelines varying in composition from *q* to *h*. All mixtures in the area *pehq* consist, at 1,164° C., of these two phases, as shown by the tie-lines.

The relationships in the field of carnegieite are shown in the enlarged and distorted diagram Figure 13, *a*. The liquid *e* is in equilibrium with nepheline *h* and carnegieite *i*. The one-phase area of ternary carnegieite solid solutions *inm* is

much smaller than in the preceding diagrams, and at a temperature 1° lower the area diminishes to a point.

THE $1,123^\circ\text{C.}$ ISOTHERM (FIG. 14)

This isothermal plane shows the phase relations at a temperature just above the ternary eutectic (E in Fig. 7). At this temperature there are two one-phase (liquid) areas in the system due to the

with nepheline of composition varying from r to s .

The liquids w , x , and y are each in equilibrium with two solid phases. Liquids of composition between w and x are each in equilibrium with wollastonite. Liquids of composition between x and y are each in equilibrium with nepheline varying in composition from q to r . Liquids varying in composition from y

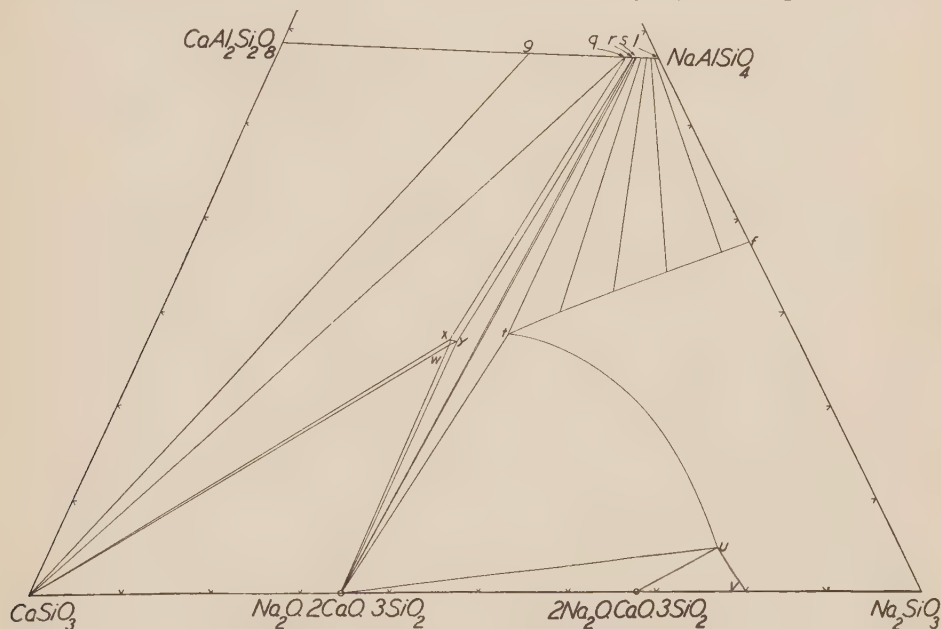


FIG. 14.—The phase relations at $1,123^\circ\text{C.}$

presence of a maximum temperature on the boundary curve between the fields of nepheline solid solution and the $1:2:3$ compound. Carnegieite no longer exists at this temperature.

The $2:1:3$ compound is stable at this temperature and is in equilibrium with liquid of composition varying from u to v . All mixtures in the area $2:1:3\text{--}u\text{--}v$ consist of the $2:1:3$ compound and liquid.

The liquid v is in equilibrium with both $1:2:3$ and $2:1:3$. Similarly, liquid t is in equilibrium with $1:2:3$ and nepheline of composition s .

The $1:2:3$ compound is in equilibrium

to w are in equilibrium with the compound $1:2:3$.

Other areas in this figure have the same properties as their analogues in the isothermal diagrams already described. It may be mentioned that the three-phase area representing the equilibrium between wollastonite, nepheline q , and liquid x is much larger than the analogous area in Figure 12.

THE SOLID-PHASE RELATIONS

Figure 15 shows the solid-phase relations in the system. The quadrilateral is divided into a series of alternating two-

and three-phase areas, which indicate the final products of crystallization of all mixtures whose compositions lie within the system.

A mixture whose total composition lies in a three-phase area will, upon solidification, consist of the three phases which form the apexes of that triangle.

Mixtures whose total compositions lie in a two-phase area will, upon solidifica-

wollastonite-sodium metasilicate may be discussed with the aid of Figure 16.

THE FIELDS OF NEPHELINE AND CARNEGIEITE

A mixture of composition *o* will at $1,340^{\circ}\text{C.}$ yield carnegieite solid solution of composition poorer in sodium metasilicate than *p*. With falling temperature, the liquid will change composition along a curved course *oq*, and the composition

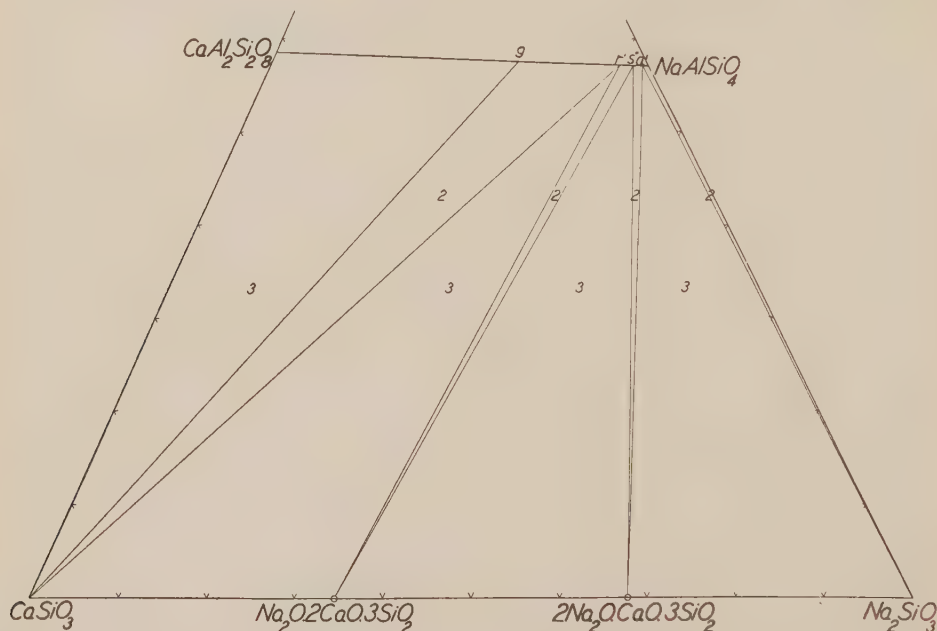


FIG. 15.—The solid-phase relations. The numbers 2 and 3 signify two- and three-phase areas, respectively

tion, consist of two phases—a phase of fixed composition and a solid solution whose composition is given at the end of the tie-line joining the fixed phase and the composition point of the mixture.

This diagram shows that pure nepheline cannot coexist with a lime-bearing compound, for there is always anorthite in solid solution in the nepheline when lime occurs in the system.

COURSES OF CRYSTALLIZATION

The courses of crystallization within the various fields of the system nepheline-

of the carnegieite will change until the liquid reaches the point *q* ($1,241^{\circ}\text{C.}$). At this temperature the liquid will have the composition *q*, and the carnegieite the composition *p*, with *qp* the tie line passing through the initial composition point *o*. The inversion of carnegieite to nepheline begins at this temperature, and the first nepheline crystals have the composition *u*. With falling temperature the composition of the liquid changes in the boundary curve, and the composition and proportions of both nepheline and carnegieite change until the point *q'* is

reached ($1,232^{\circ}\text{C}.$). Inversion of carnegieite to nepheline is completed at this temperature, since the tie-line $q'u'$ passes through the initial composition point o . The composition of the last trace of carnegieite is p' and that of nepheline is u' , and the liquid has the composition q' . It should be noted that with falling temperature the carnegieite becomes richer in sodium metasilicate, while the nephe-

boundary kt (of the yr type in Fig. 14) passes through the initial composition point o . With falling temperature the liquid k will move down the boundary curve to the reaction point R , yielding 1:2:3 crystals and nepheline whose composition changes from t to s'' . At the reaction point R the liquid has the composition R ; nepheline, the composition s'' ; and the liquid and 1:2:3 react to

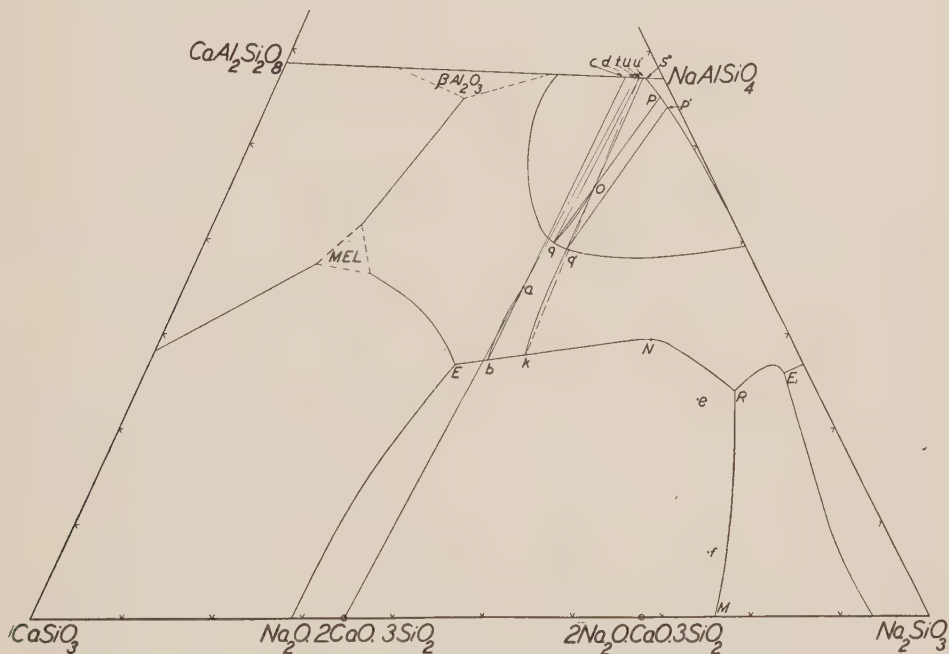


FIG. 16.—Equilibrium crystallization in the system $\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$. The abbreviation *MEL* signifies mellite.

line solid solution contains less anorthite. With continued cooling the liquid q' will leave the boundary curve and follow a curved course $q'k$ to the boundary curve between the fields of nepheline and 1:2:3. The course is necessarily curved, since the composition of the nepheline changes continually; and it is probable that nepheline becomes slightly richer in anorthite with falling temperature. At point k on the boundary curve (temperature 1,118° C.) the nepheline has the composition t , since the three-phase

precipitate more nepheline of the same composition and the 2:1:3 compound, until the liquid is used up. The composition of the initial mixture o lies in the triangle 1:2:3, 2:1:3, and nepheline s'' (Fig. 15), so that the final products of crystallization are these three phases. The content of anorthite in the nepheline solid solutions decreases during the inversion interval; then it increases as the liquid follows a curved course to the boundary curve, and then decreases again as the liquid moves down the boundary

curve. There is no means of determining the extent of this change in composition, but such behavior must be inferred from theoretical considerations.

The liquid *a* will begin to crystallize at a temperature of $1,200^{\circ}\text{C}$. with the separation of nepheline solid solution containing less anorthite than *c*. The liquid will follow a curved course *ab* to the boundary curve, the nepheline becoming richer in anorthite; and when the liquid has the composition *b*, the nepheline has the composition *c*, for the tie-line *bc* (of the type *yr* in Fig. 14) passes through the initial composition point *a*. With cooling, the liquid *b* will move down the boundary curve, yielding nepheline solid solutions and crystals of the 1:2:3 compound. The nepheline solid solutions change in composition and contain less anorthite. Crystallization is complete when the three-phase boundary 1:2:3-*d* (of the type 1:2:3-*s* in Fig. 14) passes through the initial composition point *a*. This three-phase boundary is the base of a three-phase triangle (of the type *s-t*-1:2:3 in Fig. 14) in which the apex is a liquid in the boundary curve between the fields of nepheline solid solution and 1:2:3. The apex of the triangle represents the composition of the last minute quantity of liquid as the mixture becomes crystalline. The final products of crystallization are crystals of 1:2:3 and nepheline of composition *d*.

Crystallization of other mixtures in the fields of nepheline and carnegieite are similar to those already described. The final products of crystallization will consist of either two or three solid phases, depending upon whether the initial composition of the mixture lies in a two- or phase area, as shown in Figure 15.

CRYSTALLIZATION IN THE OTHER FIELDS

The crystallization of liquids whose initial compositions lie in the fields of

pseudowollastonite, 1:2:3, 2:1:3, or sodium metasilicate will be outlined briefly with the aid of Figures 15 and 16.

All liquids in the field of pseudowollastonite begin crystallization with that compound as the primary phase and the composition of the liquid changes directly away from the pseudowollastonite apex. The liquid will encounter the boundary curve of the field of 1:2:3, or the field of nepheline solid solutions, depending upon the initial composition point within the pseudowollastonite field, and one of these compounds will separate as the secondary phase. If nepheline is the secondary phase, its composition will be richer in anorthite than *r'* when the boundary curve is encountered, and the approximate composition may be determined from the tie-lines of Figure 13. The liquid will become completely crystalline at the ternary eutectic *E*, yielding the phase assemblage wollastonite, nepheline *r'*, and 1:2:3. All liquids in the field of pseudowollastonite become completely crystalline at the ternary eutectic *E*, for the field lies within the three-phase area CaSiO_3 -1:2:3-nepheline *r'* (Fig. 15). It should be noted that the inversion of pseudowollastonite to wollastonite will take place at $1,125^{\circ}\text{C}$. before the liquid encounters the ternary eutectic.

Liquids in the field of the 1:2:3 compound will yield a number of different phase assemblages upon crystallization, depending upon the two- or three-phase area in which the initial composition point lies. If the initial composition point lies in the triangle wollastonite-nepheline *r'*-1:2:3 (Fig. 15), crystallization is completed at the ternary eutectic *E*; and these three phases are the final crystalline products. Liquids in the area 1:2:3-*r'*-*s''* (Fig. 15) will yield crystals of the 1:2:3 compound and a nepheline of composition between *r'* and *s''*; the liquid

moves down the boundary curve between the two fields toward the reaction point R , and crystallization is complete when the base of a three-phase triangle (of the type $s\text{--}t\text{--}1:2:3$ in Fig. 14) passes through the initial composition point. All liquids whose compositions lie in the three-phase area $s''\text{--}1:2:3\text{--}2:1:3$ (Fig. 15) will be used up at the reaction point R and will yield those phases as the final products of crystallization.

Certain liquids in the field of $1:2:3$ will not yield this compound as a final product of crystallization. This is due to the presence of the incongruent compound $2:1:3$ in the field of $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$. All mixtures in the two-phase area $2:1:3\text{--nephelines } s'' \text{ to } a'$ (Fig. 15) will yield $2:1:3$, and a nepheline of composition determined by the tie-line which passes through the initial composition point. This tie-line is the base of a three-phase triangle whose apex is a liquid in the boundary curve between the fields of nepheline and $2:1:3$.

The three-phase area $2:1:3\text{--sodium metasilicate--nepheline } a'$ (Fig. 15) includes mixtures whose compositions lie in the fields of $1:2:3$, $2:1:3$, and sodium metasilicate. For all these compositions the final products of crystallization will be sodium metasilicate, $2:1:3$, and nepheline solid solution of composition a' . Mixtures in the fields of $2:1:3$ and sodium metasilicate exhibit simple subtraction relations, with cooling; and their crystallization courses require no further discussion. The crystallization of liquids whose compositions lie in the $1:2:3$ field of this three-phase area exhibit reaction relations, which may be illustrated by considering the crystallization of two typical mixtures.

A liquid of composition e (Fig. 16) yields $1:2:3$ as the primary phase and moves directly away from the $1:2:3$ composition point until the boundary

curve of the field of nepheline is encountered. The first crystals of nepheline that are precipitated have a composition slightly richer in anorthite than nepheline s'' . The liquid follows the boundary curve yielding crystals of $1:2:3$ and nepheline solid solutions of decreasing anorthite content. When the liquid reaches the reaction point R , nepheline has the composition s'' . The temperature remains constant while liquid and $1:2:3$ crystals react to form $2:1:3$ and nepheline s'' . With the disappearance of the $1:2:3$ crystals a univariant equilibrium condition again exists, and with further cooling the liquid follows the boundary curve between the fields of $2:1:3$ and nepheline, precipitating these two phases. The nepheline solid solutions change continually and contain less anorthite than nepheline s'' . When the liquid reaches the ternary eutectic E_1 , the nepheline has the composition a' (Fig. 15). Sodium metasilicate separates together with $2:1:3$ and nepheline a' until crystallization is complete. This crystallization is typical of all mixtures within the area $2:1:3\text{--}N\text{--}R$ (Fig. 16).

The liquid f separates $1:2:3$ as the primary phase, moving directly away from that compound until the boundary curve of the field of $2:1:3$ is encountered. The liquid follows the boundary curve separating $2:1:3$ and resorbing $1:2:3$ crystals until the latter are completely dissolved. This condition obtains when a line passing through the $2:1:3$ compound and the initial composition point, f , intersects the boundary curve. The liquid then leaves the boundary curve and moves across the field of $2:1:3$ with the separation of that phase, until the boundary curve of sodium metasilicate is encountered. Sodium metasilicate and $2:1:3$ separate as the liquid moves down the boundary curve to the ternary eutectic E_1 . At the eutectic, nepheline of composition a' (Fig. 15)

crystallizes together with sodium metasilicate and 2:1:3 until the liquid is used up. This crystallization is typical of mixtures in the area $M-R-2:1:3$ (Fig. 16).

FRACTIONAL CRYSTALLIZATION

Fractional crystallization of liquids within the system may be described with the aid of Figure 17. The perfect fractionation curves for liquids in the fields

temperature on the boundary curve between the fields of nepheline solid solutions and the 1:2:3 compound.

In the area to the left of the tie-line joining the 1:2:3 compound with the maximum temperature A and the fractionation curve ABC , liquids reach the ternary eutectic E . The products of crystallization do not differ appreciably from those obtained under equilibrium



FIG. 17.—Fractional crystallization in the system $\text{NaAlSiO}_4\text{--CaSiO}_3\text{--Na}_2\text{SiO}_3$. The abbreviation *MEL* signifies melilite.

of nepheline and carnegieite solid solutions are a series of reverse curves emanating from the NaAlSiO_4 apex. Their reverse character is due to the presence of different compounds in solid solution in the low- and high-temperature modifications of NaAlSiO_4 . With the failure of equilibrium, liquids of the system will complete their crystallization at one of the ternary eutectics, E or E_1 . The goal that is attained is governed by the location of the initial composition point with respect to the maximum

conditions; the difference is that there will be a range of nepheline solid solutions in the final crystalline product.

In the area to the right of the fractionation curve CBA and the tie-line joining the 1:2:3 compound with the maximum temperature A , the ultimate goal of fractional crystallization is the ternary eutectic E_1 . All liquids whose initial compositions lie in the area will reach this goal, for with the failure of equilibrium no reaction occurs at the invariant point R , and liquids that reach R con-

tinue down the boundary curve to E_1 . The product of crystallization would consist of 1:2:3, nepheline solid solutions, 2:1:3, and sodium metasilicate.

Liquids that reach the boundary curve MR do not follow that curve but move across the field of 2:1:3 along courses shown in Figure 17. The liquids reach the boundary curve between 2:1:3 and nepheline or sodium metasilicate and follow the curve to the eutectic E_1 . The final products of crystallization are again 1:2:3, 2:1:3, nepheline solid solutions, and sodium metasilicate.

Fractional crystallization in the system reduces the variety of phase assemblages that result from complete crystallization of mixtures but increases the number of phases occurring in the final product. The residual liquids that reach the eutectic E_1 are characterized by an impoverishment in lime and an enrichment in soda-alumina silicates.

PETROLOGIC SIGNIFICANCE

No new ternary compounds were encountered in the system, and no quaternary fields encroached upon this portion of the plane. The equilibrium relations in the system are ternary; and, although the composition of nepheline and carnegieite solid solutions can be expressed in terms of the three components— NaAlSiO_4 , CaSiO_3 , and Na_2SiO_3 —if the proportion of the latter is considered a negative quantity, it is more convenient to express the compositions in terms of the compounds $\text{CaSiO}_3\text{--CaAl}_2\text{Si}_2\text{O}_8\text{--NaAlSiO}_4\text{--Na}_2\text{SiO}_3$. The four compounds all lie in the same plane and are related to each other in the manner of reciprocal salt-pairs.

Compositions within the system, and the mineralogical assemblages, do not, in general, approximate those obtained in igneous rocks. Nepheline occurs as a primary constituent in many alkaline

rocks, and in some instances wollastonite is associated with it—although in very minor quantities. O. H. Erdmannsdörfer¹¹ describes two rock types from the East African Rift—a wollastonite urtite and a wollastonite ijolite—in which wollastonite occurs in unusual abundance. In the former rock the mode contains approximately 72 per cent wollastonite, 24 per cent nepheline, and 4 per cent perovskite. The textural relations of the minerals revealed that perovskite developed distinct octahedral outlines and that wollastonite formed earlier than nepheline, although their crystal outlines were not well developed. The crystallization of wollastonite as an early mineral is to be expected in a mixture of this composition. The rock types described by Erdmannsdörfer were obtained from ejected volcanic blocks, and no occurrences *in situ* of such wollastonite-rich rocks have ever been found. He does, however, mention certain lavas, in the same locality, which contain phenocrysts of nepheline and aegirine-augite with rarer wollastonite.

THE POSITION OF THE TERNARY EUTECTICS

Equilibrium studies of various systems containing lime, magnesia, iron oxide, alumina, soda, potash, and silica in proportions such as to give standard rock-forming minerals have shown that fractional crystallization tends to result in a concentration of alkali-alumina silicates in residual liquids.¹² Similar results are obtained in the system herein studied, and both equilibrium and fractional crystallization yield residual liquids that

¹¹ "Über Wollastoniturtit und die Entstehungsweisen von Alkaligesteinen," *Sitzungsber. Heidelb. Ak. d. Wiss.* (1935), pp. 1-23.

¹² Bowen, "Recent High-Temperature Research on Silicates and Its Significance in Igneous Geology," *Amer. Jour. Sci.*, Vol. XXXIII (5th ser., 1937), pp. 1-21.

are impoverished in lime and enriched in soda-alumina silicates. The lowest-melting liquid is at the eutectic E_1 (Fig. 7) and contains less than 3 per cent of the wollastonite molecule. The ternary eutectic E , between wollastonite, nepheline solid solution, and 1:2:3, lies at a much higher temperature; but again the low-melting liquid tends toward an impoverishment in lime, for the crystalline product contains about 10 per cent of the CaSiO_3 molecule.

THE RARITY OF PURE END MEMBERS OF SOLID-SOLUTION SERIES

Rock-forming minerals, with the exception of quartz, are all members of solid-solution series. It is well known that pure-end members of solid-solution series are rarely, if ever, found in nature. Evidence from equilibrium investigations likewise indicates that pure end members of solid solution series are not formed in synthetic melts when there are substances present with which they may form solid solutions.

The system herein studied reveals that pure nepheline does not exist in the presence of a lime-bearing compound. Pure nepheline cannot coexist with wollastonite, for reaction occurs between the two compounds to produce anorthite and sodium metasilicate, and the former enters into solid solution in nepheline. The nepheline solid solution which coexists with wollastonite has a minimum anorthite content of 8 per cent. Similarly, the compounds 1:2:3 and 2:1:3 do not coexist with pure nepheline but are in equilibrium with nepheline solid solutions containing about 4 per cent and 1 per cent of anorthite, respectively.

Chemical analyses of natural nephelines indicate that their anorthite content varies from 0 to 15 per cent. Bowen¹³

¹³ "The Sodium-Potassium Nephelites," *ibid.*, Vol. XLIII (1917), pp. 115-32.

compared the analyses of several typical nephelines and found that when the anorthite content of nepheline was high there was a tendency toward a low albite content, and vice versa. The inference was that nephelines containing a high albite content were formed from solutions containing sodic plagioclase, and in the case of a high anorthite content the nephelines were formed from solutions of a calcic plagioclase. Evidence of a similar nature was obtained in this system, for the nepheline solid solution in equilibrium with wollastonite has a much higher minimum anorthite content than the nepheline in equilibrium with the soda-rich lime compound, $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$.

Other high-temperature investigations have shown that, when lime is present in mixtures containing the albite molecule, some anorthite is produced by reaction and a plagioclase is formed. This reaction effect has been obtained by Schairer and Bowen,¹⁴ in the system albite-diopside; by A. T. Prince,¹⁵ in the system albite-sphene; and by Foster,¹⁶ in the system wollastonite-albite.

CRYSTALLIZATION IN THE SYSTEM WOLLASTONITE-NEPHELINE AND THE SYSTEM ANORTHITE-WOLLASTONITE-NEPHELINE

It has been mentioned in the "Introduction" that mixtures in the system nepheline-wollastonite and certain mixtures of the system wollastonite-anorthite-nepheline do not crystallize within the confines of their systems, as a result of the enrichment of the liquid in sodium metasilicate. The products of crystallization can be readily determined with the aid of Figure 15.

¹⁴ Unpublished data.

¹⁵ "The System Albite-Anorthite-Sphene," *Jour. Geol.*, Vol. LI (1943), pp. 1-16.

¹⁶ See fn. 3 (1942).

On the join nepheline-wollastonite, initial mixtures containing up to 90 per cent of nepheline will yield wollastonite, nepheline solid solution containing 8 per cent of anorthite, and 1:2:3, as final products. Mixtures containing over 91 per cent nepheline will yield phase assemblages consisting of two or three crystalline products, depending upon the two- or three-phase area in which the composition of the mixture lies. These phase assemblages are: nepheline solid solution and 1:2:3; nepheline solid solution, 1:2:3 and 2:1:3; nepheline and 2:1:3; nepheline, 2:1:3 and sodium metasilicate; or nepheline and sodium metasilicate. Thus six different phase assemblages are possible products of crystallization of mixtures on the join nepheline-wollastonite which one might expect to constitute a simple system; only one of these assemblages contains wollastonite as a constituent. With fractional crystallization all mixtures containing over 91 per cent nepheline yield sodium metasilicate in the final product.

In the triangle wollastonite-anorthite-nepheline, mixtures with small amounts of wollastonite and anorthite, as plotted in that triangle, will not yield these phases in the final product of crystallization. Six different phase assemblages result from equilibrium crystallization of liquids which pass out of the initial triangle and enter the triangle nepheline-wollastonite-sodium metasilicate. The composition of these phase assemblages depends upon the location of the initial composition point with respect to the two- and three-phase areas as shown in the solid-relations diagram (Fig. 15). Again, with fractional crystallization, all mixtures that do not reach the ternary eutectic *E* yield sodium metasilicate in the final crystallization product.

The enrichment of the residual liquids in sodium metasilicate is analogous to the

natural processes in which highly sodic liquids may be concentrated near the close of the period of magmatic crystallization, and such processes are often considered as the explanation of the late-stage albitization phenomena observed in many acid and basic igneous rocks.¹⁷

THE CHEMICAL SIMILARITY BETWEEN $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ AND PECTOLITE

Although 1:2:3 and pectolite are not correlative in optical and crystallographic properties, there is a chemical similarity between the two, and there is a certain parallelism between the association of wollastonite and pectolite in nature and the association of CaSiO_3 and 1:2:3 in the system. Pectolite has the molecular proportions $\text{H}_2\text{O} \cdot \text{Na}_2\text{O} \cdot 4\text{CaO} \cdot 6\text{SiO}_2$, and this may be regarded as the equivalent of $2(\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2)$ with the replacement of one Na_2O by one H_2O molecule. Pectolite has natural occurrences and associations that are similar to those of wollastonite. The field of the 1:2:3 compound is adjacent to that of CaSiO_3 in the system, and the two are associated with nepheline at the ternary eutectic *E* (Fig. 7).

In natural occurrences, pectolite has been reported as a minor constituent of nepheline-bearing rocks. Thus, S. J. Shand¹⁸ has described wollastonite-pectolite in the foyaites of Sekukuniland, in quantities varying from 0 to 6 per cent.

¹⁷ E. B. Bailey and G. W. Grabham, "Albitization of Basic Plagioclase Feldspars," *Geol. Mag.*, Vol. VI (1909), pp. 250-56; G. H. Anderson, "Granitization, Albitization, and Related Phenomena in the Northern Inyo Range of California-Nevada," *Bull. Geol. Soc. Amer.*, Vol. XLVIII (1937), pp. 1-74; R. J. Colony, "The Final Consolidation Phenomena in the Crystallization of Igneous Rocks," *Jour. Geol.*, Vol. XXXI (1923), pp. 169-78.

¹⁸ "The Nepheline Rocks of Sekukuniland," *Trans. Geol. Soc. So. Africa*, Vol. XXIV (1921), pp. 111-49.

The optical properties of the mineral showed certain characteristics of wollastonite, and others which were similar to pectolite, so that Shand suggested the use of the double name until more definite evidence could be obtained. Shand mentions a similar occurrence of a pectolite mineral in the lujaurites in Pilandsberg which were described by Brouwer.

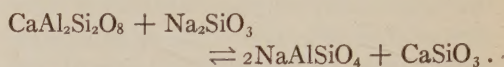
Perhaps pectolite is produced in natural rocks by fractionation effects similar to those whereby 1:2:3 is formed in the present system, but in the natural magmas the presence of water induces formation of the hydrous phase.

THE WOLLASTONITE-ANORTHITE-NEPHELINE-SODIUM METASILICATE
EQUILIBRIUM

The equilibrium relations in the quadrilateral wollastonite-anorthite-nepheline-sodium metasilicate provide evidence concerning the formation of nepheline-bearing rocks as a result of reaction between residual liquids and certain crystalline phases in the magma.

In order to simplify the discussion of the equilibrium relations, it is convenient to neglect the presence of the compounds 1:2:3 and 2:1:3 and to consider only the quadrilateral formed by the four compounds. The compounds at the ends of the diagonals may be taken to represent reciprocal salt-pairs,¹⁹ each of which may undergo partial double decomposition to form the other pair. In this simplified view a line approximating the conjugation line, wollastonite-nepheline, would divide the quadrilateral into two parts only. The three solid-phase assemblages that would exist under this simplification would be either wollastonite-anorthite-nepheline or nepheline-wollastonite-sodium metasilicate. Sodium metasilicate and anorthite will not occur together in

any phase assemblage. The equilibrium between the salt pairs may be expressed by the equation



The reaction between anorthite and sodium metasilicate tends to destroy one of the pair with the concomitant formation of nepheline and wollastonite. However, the reaction does not go to completion, and some anorthite enters into the nepheline mix-crystals. For this reason the conjugation line in the system is $\text{Ne}_{92}\text{An}_8$ -wollastonite instead of the join between the latter and pure nepheline.

Shand²⁰ has postulated this reaction for the formation of nepheline, and the present investigation indicates that such a reaction might occur. However, Shand believes that the sodium metasilicate content of the residual liquid results from reaction between limestone and magma. The present investigation shows that residual liquids become enriched in sodium metasilicate as a result of fractional crystallization, and it may be that it is sodium metasilicate liquids of this latter provenance that produce the effects Shand postulates—if, indeed, they do occur.

ACKNOWLEDGMENT.—The writer wishes to express his indebtedness to the faculty of the Department of Geology and Paleontology of the University of Chicago for the facilities provided for this research project. He is particularly grateful to Dr. N. L. Bowen for his guidance and advice during the course of the investigation.

²⁰ "Limestone and the Origin of Feldspathoidal Rocks," *Geol. Mag.*, Vol. LXVII (1930), pp. 415-27.

[EDITOR'S NOTE.—If either nepheline or pseudo-wollastonite has a composition outside the plane of Fig. 8, the maximum on their boundary curve would not have precisely the significance attached to it here or in Gummer, *Jour. Geol.*, Vol. LI (1943), p. 519.—N.L.B.]

¹⁹ A. Findlay, *The Phase Rule* (New York: Longmans, Green & Co., 1927), p. 278.

